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CHEMISTRY.—*On some new indicators for the colorimetric determination of hydrogen-ion concentration.*[1] HERBERT A. LUBS and WILLIAM MANSFIELD CLARK, Bureau of Animal Industry.

In the biochemical application of the colorimetric method of determining hydrogen-ion concentrations several difficulties are encountered. The most serious of these are the so-called protein and salt errors and the obscuring effect of the natural colors of the solutions to be tested. All of these hindrances to accurate determinations are encountered to a greater or lesser extent in applying the method to bacterial cultures and culture media. Indeed, the method in its particular application to general bacteriological problems is in a somewhat unsatisfactory condition, and we are, therefore, attempting to simplify and systematize it so that it may be used extensively in general bacteriological work.

Unsatisfactory color changes alone rule out many indicators which, though useful with perfectly clear solutions, are of little or no value in bacteriological media; and, as Sörensen[2] has shown, the great majority of indicators listed in the elaborate tables of Salm, Thiel, and others must be rejected for one reason or another.

[1] From the research laboratory of the Dairy Division, Bureau of Animal Industry. Published by permission of the Secretary of Agriculture.

[2] Biochem. Zeitschr. **21**: 131. 1909; **22**: 352. 1909; Ergebn. d. Physiol., **12**: 393. 1912.

Sörensen has done invaluable service by eliminating from these tables the comparatively useless indicators and in his excellent résumé he has offered a selection of undoubted value. Unfortunately some of these are of little value in bacteriological media and others, from our experience, might be replaced with advantage. The eliminations leave some serious gaps in the series. There are, however, some indicators which have been studied since Sörensen's compilation, a few of which have not been investigated with reference to their applicability for determining hydrogen-ion concentration, and there also remain the possibilities in new syntheses, as Sörensen has suggested.

Walpole[3] in a recent article gives an excellent résumé of the method and suggests some new indicators. Those suggested are either not particularly satisfactory for our purpose or are rather difficult to obtain or prepare.

These considerations have led us to the investigation and compilation herein recorded. A more detailed account of the usefulness of particular indicators, of their protein and salt errors, the determination of their apparent dissociation constants, and our attempts to systematize the method for the general use of the bacteriologist will be reserved for subsequent papers. This paper is to be regarded merely as a preliminary description of our work in this field.

The importance of a simple, accurate, and well-systematized colorimetric method of determining the hydrogen-ion concentrations of bacteriological culture media and cultures has been pointed out in previous papers[4] from this laboratory.

PREPARATION AND PROPERTIES OF INDICATORS OF THE METHYL RED TYPE

Methyl Red, *o*-Carboxybenzene-azodimethylaniline, $N(CH_3)_2—C_6H_4—N_2—C_6H_4COOH$, was first prepared by Rupp and Loose.[5] Tizard[6] later improved the method of preparation so that almost quantitative yields were obtained. He determined its apparent dissociation constant

[3] Biochem. Journ. **8**; 628. 1914.

[4] Journ. Infect. Diseases **17**: 109. 1915; ibid. **17**: 160; Journ. Biol. Chem. **22**: 87. 1915.

[5] Ber. d. deutsch. Chem. Ges. **41**: 3905. 1908.

[6] Trans. Lond. Chem. Soc. **97**: 2477. 1910.

as an acid and found the value, $K = 1.05 \times 10^{-5}$ at 18°. Palitzsch[7] states that the region in which methyl red can be used for colorimetric determination of hydrogen-ion concentration lies between P_H^+ 4.2 and P_H^+ 6.3, and that in this region a difference of 0.1 in the P_H^+[8] value produces a marked difference in the tint of the indicator. He also determined its so-called protein and salt errors. The range of color extends from yellow on the alkaline side to red on the acid side. The brilliant and sharp changes of methyl red and its utility in the presence of protein and protein cleavage products makes it an excellent indicator for the estimation of the hydrogen-ion concentration of bacteriological media.

It was with the hope of finding an indicator showing color changes at hydrogen-ion concentrations just below those which can be determined by methyl red that we began to synthesize other indicators of this series. In our bacteriological work we found that it was necessary to have an indicator which would give a fairly sharp differentiation between P_H^+ 6 and P_H^+ 6.5. Para nitrophenol is an excellent indicator for this range in a colorless solution, but unfortunately its color change is of such a nature that it is obscured by the natural color of most bacteriological media.

We found by varying the substituent alkyls in the aniline residue of methyl red that the resulting indicators show but little difference in properties. Their colors vary only in intensity, and the hydrogen-ion concentrations at which the changes occur differ but little. As would be expected, the indicators with two substituent alkyls had a much deeper color than the corresponding monoalkyl derivatives.

INDICATORS OF THE METHYL RED TYPE INVESTIGATED

Monomethyl Red, o-Carboxybenzene-azomonomethylaniline.—A specimen of this material was kindly sent to us by Dr. L. W. Jones. This was recrystallized from alcohol. The nature of the color change was practically the same as that of methyl red but far less intense. Changes occur over the range P_H^+ 4.25 to P_H^+ 6.00.

Methyl Red, o-Carboxybenzene-azodimethylaniline.—Previously described.

Monoethyl Red, o-Carboxybenzene-azomonoethylaniline.—This indicator was prepared from anthranilic acid and monoethylaniline by the

[7] C. R. d. trav. d. Lab. Carls. **10**: 163. 1911.

[8] $P_H^+ = \log \frac{1}{C_H}$. For a discussion of the significance and convenience of this symbol see Sorensen, loc. cit.

method of Tizard for the analogous methyl red. It was recrystallized from alcohol. Color changes occur over the range P_H^+ 4.25 to P_H^+ 6.00.

Diethyl Red, o-Carboxybenzene-azodiethylaniline.—This substance was prepared from anthranilic acid and diethyl aniline by the method previously described. It was recrystallized from alcohol. Its colors are slightly deeper than those of methyl red and the changes occur over the range P_H^+ 4.50 to P_H^+ 6.50.

Monopropyl Red, o-Carboxybenzene-azomonopropylaniline.—This indicator was prepared from anthranilic acid and monopropyl aniline. Color changes are from yellow to red and extend over the range P_H^+ 4.25 to P_H^+ 6.25.

Dipropyl Red, o-Carboxybenzene-azodipropylaniline.—Attempts to prepare this substance in the manner described by Tizard for methyl red were not successful, so the following procedure was adopted: Five grams of anthranilic acid were dissolved in two molecular equivalents of 3N hydrochloric acid. To the cooled solution was added the necessary amount of sodium nitrite solution. Starch-potassium-iodide paper was used as the indicator. The diazotized solution was allowed to stand in ice water for one-half hour and then 6.6 grams of dipropyl aniline dissolved in 150 cc. of alcohol were added. The mixture was allowed to stand in the ice water for two hours, and then at room temperature over night. The next morning the bluish purple crystals were filtered off with suction, washed with a little cold alcohol and then with water. The yield, after drying in the air, was about 3 grams. Color changes are from reddish-violet to yellow and occur over the range P_H^+ 4.50 to P_H^+ 6.50. They are slightly more intense than in the corresponding diethyl compound.

Dimethyl-α-naphthylamine Red, o-Carboxybenzene-azodimethyl-α-naphthylamine.—Howard and Pope[9] first made this indicator. Their method of preparation was used and an almost quantitative yield was obtained. The color changes are extremely brilliant from purple to yellow and occur over the range P_H^+ 4.50 to P_H^+ 6.50.

The phenyl-α-naphthylamine, α-napthylamine, and diphenylamine derivatives of this series were also prepared by Howard and Pope. We investigated the two latter compounds and found that the color changes were not very brilliant and probably would be of little use in bacteriological work.

The color changes of *o*-Carboxybenzene-azodimethyl-α-naphthylamine take place between P_H^+ 5.00 and P_H^+ 6.75. The changes of the

[9] Trans. Lond. Chem. Soc. **99**: 1333. 1911.

diphenylamine compound occur between P_H^+ 4.25 and P_H^+ 5.50. A cold saturated alcoholic solution of these two indicators was used. In all other cases a solution of 0.1 gram of indicator in 300 cc. alcohol and 200 cc. distilled water was used.

INDICATORS OF THE SULPHONE-PHTHALEIN TYPE

Phenolsulphonephthalein was first prepared by Remsen and Sohon[10] by the condensation of phenol and the anhydride of *o*-sulphobenzoic acid. An improved method which has been used in this laboratory is based upon the action of phenol upon the chloride of *o*-sulphobenzoic acid in the presence of anhydrous zinc chloride. By the old method a large amount of alkali insoluble material is obtained, while by the new method practically none is formed. An additional advantage of the new method lies in the greater ease with which the starting materials can be prepared.

PHENOLSULPHONE-PHTHALEIN

Preparation.—The starting material was pure saccharin. From this the ammonium salt of *o*-sulphobenzoic acid was prepared by substantially the same method as described by Remsen and Holmes.[11] The chloride was prepared from the ammonium salt as described by Remsen and Dohme.[12] Ten grams of the acid chloride, 15 grams of phenol and 10 grams of freshly fused and pulverized zinc chloride were mixed in a porcelain jar. As soon as the zinc chloride was added a vigorous evolution of hydrochloric acid gas occurred and the temperature of the reacting mass rose spontaneously to about 55° C., developing a deep red color. The temperature was raised to 140° C. and held there for six hours. During the heating the mass was frequently stirred with the thermometer used to indicate the temperature. The reaction product gradually became more viscous. When the heating was finished the melt was disintegrated with hot water, boiled for a few minutes and filtered with suction. After a thorough washing a bright red powder was obtained. This was then dissolved in strong alkali, the solution filtered and slowly poured into hot dilute hydrochloric acid, with constant stirring. After boiling for a few minutes the flask containing the sulphonephthalein was allowed to stand for several hours, and then the indicator was filtered off with suction, washed and air dried. Com-

[10] Amer. Chem. Journ. **20**: 257. 1898.
[11] Amer. Chem. Journ. **25**: 205. 1901.
[12] Amer. Chem. Journ. **11**: 332. 1889.

plete drying can be secured at 120° C. The indicator obtained by this procedure is quite pure.

Properties.—Levy, Rowntree and Marriot[13] were the first to recognize the excellence of phenolsulphone-phthalein as an indicator for the colorimetric determination of hydrogen-ion concentration. A complete discussion of the theory of color changes of this compound will shortly be published by White and Acree. The range of color changes is from yellow to reddish-violet and extends from P_H^+ 6.50 to P_H^+ 8.50. Between P_H^+ 7 and P_H^+ 7.50 extremely sharp differentiations can be secured but the indicator can be used with entire satisfaction over the wider range. A solution of the sodium salt in water is used and such a solution can now be purchased from any of the dealers in chemical supplies. A 0.01 per cent solution is satisfactory for colorimetric purposes. Use 4–6 drops.

o-CRESOLSULPHONE-PHTHALEIN

Preparation.—This indicator was also prepared by Remsen and Sohon.[14] The method of preparation used in this laboratory was, in general, the same as that used for the analogous phenol compound. Ten grams of *o*-cresol, 15 grams of the acid chloride and 10 grams of freshly fused and pulverized zinc chloride were heated together for 6 hours at 165°–170°. The melt was then treated as previously described. The filtration is much more difficult than in the case of the phenol compound. Yield about 10 grams. *o*-Cresolsulphone-phthalein can be recrystallized from glacial acetic acid. It is quite soluble in alcohol.

Properties.—This indicator covers practically the same range as phenolsulphone-phthalein. The color changes are very similar. On the whole the phenol compound is superior to the cresol compound. The phenol compound can be prepared more easily and shows slightly sharper color changes. The indicator solution was prepared by dissolving 0.1 gram of indicator in 200 cc. alcohol. Use 2–4 drops.

THYMOLSULPHONE-PHTHALEIN

Preparation.—Ten grams of the acid chloride, 10 grams of freshly fused and dehydrated zinc chloride and 15 grams of thymol were heated for four hours at 140° C. with frequent stirring. The reaction mixture must be stirred constantly during the first half hour of the reaction in order to prevent a loss of material from frothing. The melt was boiled

[13] Archiv. Int. Med. **16**: 38. 1915. (See also Trans. of the Assoc. of Physicians, 1915.)

[14] Amer. Chem. Journ. **20**: 257. 1898.

with water. The dye collected as a black viscous mass at the bottom of the beaker. The water was poured off and the viscous mass which hardened upon cooling was boiled with alcohol to remove the remaining thymol. Upon cooling to room temperature the thymolsulphonephthalein was filtered off as greenish crystals. Yield about 5 grams. These crystals can be recrystallized from alcohol. (1) 0.3288 gram gave 0.1490 gram $BaSO_4$; (2) 0.4224 gram gave 0.2118 gram $BaSO_4$; S. calculated for $C_{27}H_{30}SO_5$, 6.88 per cent; S found (1) 6.21 per cent,[15] (2) 6.88 per cent.

Properties.—The color changes are from yellow to blue and take place between P_H^+ 8 and P_H^+ 9.75. The useful range lies between P_H^+ 8.00 and P_H^+ 9.50. Throughout this range the differentiations are extremely sharp. For colorimetric purposes a dilution of 0.1 gram of indicator in 200 cc. alcohol and 50 cc. water was used. Use 3–6 drops. This indicator covers practically the same range as phenolphthalein, and probably can be substituted for the latter to advantage in many cases. This point will be decided as soon as we have completed our work on the magnitude of the protein and salt errors of these new indicators.

α-NAPHTHOLSULPHONE-PHTHALEIN

Preparation.—Five grams of the acid chloride, 5 grams of freshly fused and dehydrated zinc chloride and 6 grams of α-naphthol were thoroughly mixed. The reaction began at once. A dark green melt was formed. This was heated to 70° with constant stirring and held at this temperature for about ten minutes. Upon longer heating, the dye tends to go over into a substance which is probably an oxidation product and which gives a green color in alkaline solution. The melt was extracted with water to remove the zinc chloride. The residue was then extracted thoroughly with ether in order to remove the excess of naphthol. It was then dissolved in cold alkali and the solution filtered. The indicator was reprecipitated by the addition of strong hydrochloric acid, filtered with suction, washed with water containing hydrochloric acid and air dried. When dry the indicator has a dark green color. Without further purification and after drying at 120° in vacuo, 0.5154 grams gave 0.2345 grams $BaSO_4$; 0.2736 grams gave 0.1239 grams $BaSO_4$. Theoretical for $C_{27}H_{18}SO_5$, 7.06 per cent S. Found (1) 6.24 per cent, (2) 6.21 per cent.

Properties.—The color changes are from yellow to blue over the

[15] Incomplete fusion suspected in this case. Further analyses were not made because of limited supply of indicator.

range of P_H^+ 7.50 to P_H^+ 9.00. Very sharp differentiations can be secured over this range. As an indicator solution use 0.1 gram dissolved in 50 cc. alcohol and add 150 cc. distilled water. Use 1–2 drops.

TETRABROM-PHENOLSULPHONE-PHTHALEIN

Preparation.—This compound was prepared as described by White.[16] Two grams of phenolsulphone-phthalein were suspended in 20 cc. of glacial acetic acid and to the suspension were added 10 grams of bromine dissolved in 10 cc. of glacial acetic acid. The flask was allowed to stand, with occasional shaking, for several hours and then the excess of bromine was removed by means of an air current. The precipitate was filtered off with suction, washed with cold acetic acid, recrystallized from the same and air dried.

Properties.—The color changes are from yellow to purple and occur over the range P_H^+ 3.50 to P_H^+ 4.50. The indicator solution was made by dissolving 0.1 gram in 250 cc. alcohol. Use 3–5 drops.

BROMTHYMOL-SULPHONE-PHTHALEIN

Preparation.—This indicator was prepared in the manner described for the analogous phenol compound. It is obtained as yellow granular crystals. We are investigating its chemical constitution and will publish our data shortly.

Properties.—The color changes are from yellow to blue and occur over the range P_H^+ 6.00 to P_H^+ 7.25. As an indicator solution use 0.1 gram dissolved in 250 cc. of alcohol.

Work is now in progress to prepare other new indicators of the sulphonephthalein type. We have already prepared phenol-nitrosulphone-phthalein, but have not purified it sufficiently to give an accurate description of its properties.

The authors take this opportunity to express their gratitude to Dr. L. W. Jones, Dr. S. F. Acree, and Dr. E. C. White for specimens of indicators and to Mr. H. A. B. Dunning for valuable suggestions.

SUMMARY

The following new indicators of the methyl red type have been prepared by us: Monoethyl red, diethyl red, monopropyl red and dipropyl red. Besides these new indicators we have also prepared and investigated the following indicators of the methyl red group which had been

[16] White, Disser. Univ. of Wisconsin. 1915.

previously made by others: Monomethyl red, α-naphthylamine red, dimethyl-α-naphthylamine red and diphenylamine red. The well known methyl red had been previously investigated by Palitzsch. Of these indicators the most satisfactory are those containing two substituent alkyls.

Several new indicators of the sulphonephthalein type were prepared; namely, thymolsulphone-phthalein, α-naphtholsulphone-phthalein, and bromthymol-sulphone-phthalein. An improved method of preparation for the sulphone-phthaleins is described.

The hydrogen-ion concentrations at which the color changes of the above indicators occur was determined.

The authors will shortly publish the result of their investigations on the utility of the most satisfactory of the new indicators with particular reference to their salt and protein errors and to their applicability in biochemical investigations.

PHYSICAL CHEMISTRY.—*The solubility of calcite in water in contact with the atmosphere, and its variation with temperature.* ROGER C. WELLS, Geological Survey.[1]

It is well known that even the small amount of carbon dioxide in the atmosphere is sufficient greatly to increase the solubility of calcite in water. Direct experiments on this point at temperatures above 25°C. were made by Kendall,[2] who found the solution to contain calcium equivalent to 46 parts of calcium carbonate per million at 25° and 29 parts at 50°. The partial pressure of carbon dioxide in Kendall's experiments was found by him to be 3.69×10^{-4} atmospheres.

Recently all the data on the solubility of calcite in carbonic acid water have been critically examined by Johnston,[3] and he has calculated the solubility of calcite in water at 16°, in contact with air containing certain small pressures of carbon dioxide, with the results given below.

When Kendall's results are compared with those calculated by Johnston, under similar conditions, the agreement is not as good as one could wish. Moreover, in a paper by Dubois[4] on the

[1] Published with the permission of the Director of the U. S. Geological Survey.

[2] Philos. Mag. Ser. 6, **23**: 973. 1912.

[3] Jour. Am. Chem. Soc. **37**: 2001. 1915.

[4] Proc. Sec. Sci., Amsterdam Academy, **3**: 46. 1901.

CALCULATED SOLUBILITY OF CALCITE IN WATER AT 16°C., IN CONTACT WITH AIR CONTAINING THE PARTIAL PRESSURE, P, OF CO_2 (JOHNSTON)

P	PARTS $CaCO_3$ PER MILLION	P	PARTS $CaCO_3$ PER MILLION
0.00020	55	0.00040	69
0.00025	59	0.00045	72
0.00030	63	0.00050	75
0.00035	66		

solubility of calcite in natural waters the dependence on temperature is barely mentioned.

Since data at lower temperatures are lacking, and since the variation of the solubility of calcite with temperature is a matter of great importance in geochemistry, I have carried out some new experiments designed especially to show the effect of temperature on the solubility.

The method of working consisted in agitating the solutions under investigation by a current of outdoor air for long intervals. The Jena flasks employed were kept in a thermostat while air was being passed, and, for the experiments at 1°C., they were immersed in a mixture of ice and water in a refrigerator during the whole continuation of the experiments.

The outdoor air used for stirring was filtered through cotton and washed by water. Although the carbon dioxide content of the air is known to be slightly variable,[5] this procedure must have equalized the small variations to a considerable degree. A number of careful determinations of the carbon dioxide content, made at various times, ranged from 3.02 to 3.27 parts in 10,000, with a mean of 3.18 parts. Apparently, then, equilibrium with a normal atmosphere was more nearly approached than it could be by any other simple procedure.

The Joplin calcite used had the following composition: SiO_2 0.09, MnO 0.05, FeO 0.19, CaO 55.80, MgO none, CO_2 (by difference) 43.87, sum 100.00 per cent. As far as determined calcite was the only solid phase involved, but, if a less soluble phase did in fact exist in the mixtures, the solubilities actually found would of course apply to it. The calcium content of the solutions was

[5] Letts and Blake. Sci. Proc. Roy. Dublin Soc. **9**: Pt. 2, 107. 1900.

calculated from the result of titrating about 50 cc. with 0.02 N $NaHSO_4$, using methyl orange as indicator. The solutions were slightly acid toward phenolphthalein, thus showing that the calcium was present chiefly as bicarbonate. The results are stated, however, in terms of $CaCO_3$, since that is the solid phase actually dissolved, or the phase that would be again precipitated on evaporation. Table I contains some results obtained at 1°C, when calcite in excess was added to water and air was passed through the solution for an hour or two daily.

TABLE I

CALCITE ADDED TO DISTILLED WATER AT 1°C. AND AIR PASSED DAILY

INTERVAL	PARTS $CaCO_3$ PER MILLION	INTERVAL	PARTS $CaCO_3$ PER MILLION
Start	25	22 days	72
1 day	33	27 days	76
2 days	47	30 days	74
3 days	61	32 days	75
11 days	62	34 days	75
14 days	72	50 days	76
18 days	73		

Table II shows how slowly a supersaturated solution, without points of crystallization other than the walls of the flask, loses its excess CO_2 and $CaCO_3$ at 1°. The high results of this series are probably due in part to the deposition of a more soluble form of calcium carbonate than calcite and were excluded in drawing the curve below. In Table III are shown results obtained with a similar solution but with considerable powdered calcite present to assist deposition.

TABLE II

AIR PASSED AT 1° THROUGH A SOLUTION CONTAINING CO_2 AND $Ca(HCO_3)_2$

INTERVAL	PARTS $CaCO_3$ PER MILLION	INTERVAL	PARTS $CaCO_3$ PER MILLION
Start	1000	24 days	158
1 day	999	27 days	143
3 days	880	35 days	108
5 days (plentiful crystals)	720	40 days	104
		43 days	102
13 days	240	49 days	102
15 days	193	65 days	98

TABLE III

CALCITE ADDED TO A SOLUTION CONTAINING $Ca(HCO_3)_2$ AT 1°C. AND AIR PASSED

INTERVAL	PARTS $CaCO_3$ PER MILLION	INTERVAL	PARTS $CaCO_3$ PER MILLION
8 days	119	51 days	88
13 days	111	53 days	87
21 days	98	55 days	83
32 days	94	56 days	83
39 days	90	71 days	86
43 days	90		

Tables IV and V are self-explanatory. The results of the investigation are summarized by the curve in Figure 1.

TABLE IV

CALCITE ADDED TO DISTILLED WATER AT 30°C. AND AIR PASSED

INTERVAL	PARTS $CaCO_3$ PER MILLION	INTERVAL	PARTS $CaCO_3$ PER MILLION
25 days	58	46 days	57
38 days	53	56 days	55

TABLE V

SOLUBILITIES FOUND AT OTHER TEMPERATURES

TEMPERATURE C.	PARTS $CaCO_3$ PER MILLION	TEMPERATURE C.	PARTS $CaCO_3$ PER MILLION
23°	57	21°	61
22°	57	1°	82
21°	59		

The geochemical conclusion to be drawn from the curve is, that in solutions freely exposed to the atmosphere solid calcium carbonate is considerably more soluble at low temperatures than at higher temperatures. As, however, there are many possibilities of lag in adjustment of the various equilibria involved, it is doubtless true that conditions of perfect equilibrium are seldom fully attained in nature.

Although it would take too much space to point out all the results in nature, of the variation of the solubility with temperature, one or two applications of the data may be mentioned.

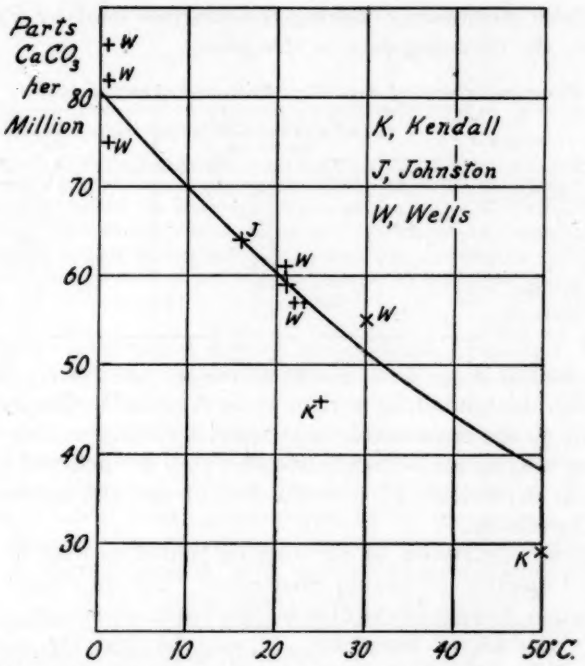

FIG. 1. Solubility of calcite in water in contact with the atmosphere, and its variation with temperature.

The Mississippi River flows, on the average, in a direction of rising temperature. Therefore, if the streams of the North become saturated with calcium carbonate, a considerable amount of it will tend to re-deposit as the river flows southward, merely because of the rise in temperature. The chemical equation is:

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

from which it follows that carbon dioxide will be again evolved as the calcium carbonate precipitates. The winds stir the atmosphere so rapidly, in comparison with the movement of the river, that it is useless to look for variations of the carbon dioxide in the atmosphere due to this cause. The water of the Mississippi, however, seems to show clearly the decrease in bicarbonate

as it flows southward. Taking the analyses used by Palmer,[6] we have the following data on this point:

Bicarbonate content of Mississippi River water at various localities

LOCALITY	PARTS OF BICARBONATE (HCO_3) PER MILLION	EQUIVALENT AMOUNTS OF $CaCO_3$
Minneapolis, Minn.	188	154
Moline, Ill.	152	125
Quincy, Ill.	175	143
Chester, Ill.	174	142
Memphis, Tenn.	135	111
New Orleans, La.	111	91

The figures in the last column above are not exactly comparable with the solubilities in pure water recorded in this paper on account of the presence of other salts, a varying acidity and a varying calcium ion concentration, but they are believed to illustrate the dependence of the solubility of calcium carbonate on the temperature.

Another application of the varying solubility may be found in the formation of marble from coral. Certain islands in the Philippines, having shores of coral, are found to consist, at fairly shallow depths, of limestone. It may be that the comparatively rapid conversion of coral into limestone is due to the fact that with every fluctuation of temperature, many particles of calcium carbonate alternately dissolve in, and re-deposit from, small amounts of water in the pore space, tending always toward the more stable calcite.

In making analyses of natural waters the temperature at the time of collection should be noted, for, although calcium carbonate may not actually deposit before the analysis can be made, owing to the slowness of the change illustrated by Table II, the question of whether the water was saturated or not when collected would require for its satisfactory answer a knowledge of its temperature.

[6] U. S. Geological Survey Bull. 479, p. 28.

ABSTRACTS

Authors of scientific papers are requested to see that abstracts, preferably prepared and signed by themselves, are forwarded promptly to the editors. Each of the scientific bureaus in Washington has a representative authorized to forward such material to this journal and abstracts of official publications should be transmitted through the representative of the bureau in which they originate. The abstracts should conform in length and general style to those appearing in this issue.

GEOLOGY.—*Some mining districts in northeastern Nevada and northwestern California.* JAMES M. HILL. U. S. Geol. Survey Bull. 594. Pp. 200. 1915.

This report embodies the results of a geologic reconnaissance which had two main objects, (1) to satisfy a present public demand for reliable information, and (2) to gather data which should be of use in preparing at a later time a general report on the geology and ore deposits of Nevada. The report brings out many facts not only of practical but of scientific interest, such as the widespread occurrence of adularia in the veins of northwestern Nevada, the presence of secondary tetrahedrite and wurtzite in the Reese River district, and the presence of selenium in the veins of Aurora.

In the region covered, sedimentary rocks ranging in age from Paleozoic to Mesozoic were noted. These sedimentary rocks, in practically every camp in which they were noted, have been intruded by granitoid rocks ranging from diorites through monzonites, quartz monzonites, and granodiorites, to granites. Their age was not definitely determined, though they cut Jurassic rocks; it is believed, however, that they were all intruded during the late Cretaceous or early Tertiary period of intrusion common to the Sierra Nevada and Great Basin province. Lava flows cover considerable parts of the region visited, particularly along the western border of Nevada and in northeast California. Farther east, in Lander County, volcanic rocks are less conspicuous.

The ore deposits are grouped as gold-silver deposits, silver-lead deposits, copper deposits, and antimony deposits. Each of these broad groups is further subdivided according to the mineral composition of the ores and their mode of occurrence.

In most of the gold-silver deposits quartz has replaced calcite gangue to some extent, giving a peculiar platy structure to the quartz. With the exception of the veins near Aurora the veins proper carry almost no sulphides although pyrite is found in the altered wall rocks. The gold is all free but usually very finely distributed. At Aurora, besides free gold, the ores carry tetrahedrite, some pyrite and chalcopyrite, and selenium. The nature of the selenium compound is not yet known.

So far as known all the silver-lead deposits are closely associated with the intrusive quartz monzonite and related rocks and are therefore of late Mesozoic or early Tertiary age. All these veins exhibit marked similarity in the sulphide minerals, though the proportions of one to another differ widely even in the same vein. Antimonial compounds, generally freibergite, are present in practically every vein. Galena, dark sphalerite, pyrite, arsenopyrite, and chalcopyrite are usually fairly abundant.

The copper deposits are associated with quartz monzonite intrusives probably of early Tertiary age. Most of them are of the contact metamorphic type or are replacement deposits in various kinds of sediments near masses of intrusive rock.

Most of the antimony deposits occur in crushed, contorted siliceous shales. The ores consist of white quartz and stibnite, with, in some places, minor quantities of tetrahedrite and galena, showing that they are probably related to the silver-lead mineralization. E. S. B.

ZOOLOGY.—*A Study of asymmetry, as developed in the genera and families of recent crinoids.* AUSTIN H. CLARK. The American Naturalist, **49**: 521–546. 1915.

Among the recent crinoids any wide departure from the normal close approximation to true pentamerous symmetry indicates unfavorable conditions of one or other of two main types, which are not mutually exclusive. These two types are: (1) *Internal unfavorable conditions*, induced by incipient phylogenetical degeneration through type-senescence, as in the Plicatocrinidæ which in the recent seas represent the almost exclusively palæozoic Inadunata; and (2) *External unfavorable conditions*, taking the form of (*a*) *Phylogenetically excessive cold* which, to cite one example, appears to be the determining factor in the asymmetry of the genus *Promachocrinus*, or (*b*) *Phylogenetically excessive warmth*, which appears to be the determining factor in the asymmetry of the Comasteridæ. A. H. C.

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